

Suppression of Fast Proton Conduction by Dilution of a Hydronium Solvate Ionic

Liquid: Localization of Ligand Exchange

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ABSTRACT

A dilution effect on the proton conduction of a hydronium solvate ionic liquid $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$, which consists of hydronium ion (H_3O^+), 18-crown-6-ether ligand (18C6), and bis[(trifluoromethyl)sulfonyl]amide anion (Tf_2N^- ; $\text{Tf} = \text{CF}_3\text{SO}_2$), has been studied. When $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$ was diluted using equimolar 18C6 solvent, the distinctive fast proton conduction in $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$ was suppressed in stark contrast to the case of common protic ionic liquids. Nuclear magnetic resonance spectroscopy showed that the fast exchange between free 18C6 molecules and coordinated ones, suggesting that the added solvent had induced a local proton exchange rather than a cooperative proton relay.

Ionic liquids (ILs) consist only of cations and anions and melt below 100 °C, which is an ultimate form of highly concentrated electrolyte solutions. They have increasingly attracted attention owing to their various uses as media for chemical, biochemical, and electrochemical reactions.¹⁻⁶ Among ILs, solvate ILs are often prepared through neutralization of Lewis acidic metal salts and Lewis basic oligoethers (glymes), where metal cations are solvated by an equimolar amount of solvents, or ligands, to give complex cations. In contrast, protic ILs are prepared through neutralization of Brønsted acids and bases, which are preferred as acid-catalyzed reaction media and fuel cell electrolytes because of the presence of acidic protons.³⁻⁶

Recently, we reported a hydronium (H_3O^+) solvate IL that is classified as both a solvate IL and protic IL. The hydronium solvate IL $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$ (18C6 = 18-crown-6-ether; Tf = SO_2CF_3) is not only the first example of a nonmetal-cation-solvate IL but also the protic IL achieving the record of the strongest Brønsted acidity among ILs.⁷ In this IL, the hydronium (H_3O^+) ion (i.e., solute ion) is solvated by 18C6 ligand (i.e., solvent) to form a $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]$ complex cation (i.e., solvate), and the counter anion is the Tf_2N^- anion.

While common protic ILs show Grotthuss-like proton conduction upon dilution, i.e., in the presence of free neutral molecules, an anomalous proton conduction has also been reported in the hydronium solvate IL $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$, where the protons of H_3O^+ move faster than the 18C6 ligand.⁸ This was the first observation of ligand exchange conduction without *free* neutral molecules, among not only solvate ILs but also protic ILs.^{8–12}

Lithium-based highly concentrated electrolytes have been widely studied in recent years.^{13–20} In some of them, Grotthuss-like fast ion conduction without free ligands has been observed.^{19,20} In the LiBF_4 and sulfolane system, for example, Li^+ ions move faster than ligands or solvent molecules, although the fast lithium conduction is suppressed by solvent addition or dilution.¹⁹ Likewise, it is interesting to study whether the dilution of $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$ by 18C6 solvent would suppress the fast proton conduction or accelerate it, as well as the dilution of common protic ILs. Additionally, study on the hydronium-based electrolytes attracts interest from the viewpoint of recently-proposed hydronium ion batteries.^{21,22}

In this work, the conduction mechanism of a diluted, or solvent-added hydronium solvate IL, i.e., $[\text{H}_3\text{O}^+ \cdot (18\text{C6})_2]\text{Tf}_2\text{N}$, has been studied in detail. ^1H and ^{19}F pulsed-field gradient

spin echo nuclear magnetic resonance (PGSE-NMR) measurements were performed to determine the self-diffusion coefficients of H_3O^+ , 18C6 ligand, and Tf_2N^- anion of the diluted hydronium solvate IL.

Experimental

Materials. 18-crown-6-ether (18C6; Kanto Chemical, 99% purity) and bis(trifluoromethylsulfonyl)imide (HTf_2N ; Kanto Chemical, 99% purity) were used without further purification. Ultrapure water was prepared using a Merck Milli-Q Reference A system.

Synthesis of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$. A hydronium solvate IL $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ was synthesized as follows. Water (0.360 g, 30 mmol) and HTf_2N (5.623 g, 20 mmol) were mixed and stirred at 400 rpm at room temperature (RT) for 1 h. Then, 18C6 (5.286 g, 20 mmol) was added and the mixture was stirred at 400 rpm at 90 °C for 2.5 h before vacuum-drying at RT for 2 h to obtain $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$. 18C6 (5.286 g, 20 mmol) was added to $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ and stirred at 400 rpm at 50 °C for 2 h for dilution.

Characterization of $[H_3O^+ \cdot (18C6)_2]Tf_2N$. The glass transition temperature of the resulting $[H_3O^+ \cdot (18C6)_2]Tf_2N$ IL was determined using a differential scanning calorimeter (DSC; Rigaku, DSC8231) with the sweeping rate of $5\text{ }^\circ\text{C min}^{-1}$.

For Raman spectroscopic measurements, an integrated Raman system (B&W Tek, InnoRam 785), consisting of a semiconductor laser light source (785 nm), an axial transmissive spectrograph, a holographic probe head, and a CCD detector, was used.

Raman spectra for $[H_3O^+ \cdot (18C6)_2]Tf_2N$ were obtained at RT, for $[H_3O^+ \cdot 18C6]Tf_2N$ at $75\text{ }^\circ\text{C}$, and for pure 18C6 at $60\text{ }^\circ\text{C}$. Infrared (IR) spectroscopic measurements were

performed at RT using a JASCO FT/IR-460 plus system. Here, $[H_3O^+ \cdot (18C6)_2]Tf_2N$ was directly put on the barium fluoride window, while $[H_3O^+ \cdot 18C6]Tf_2N$ or pure 18C6 was mixed with Nujol and hexachlorobutadiene and painted on the barium fluoride window.

A set of nuclear magnetic resonance (NMR) spectra, i.e., ^1H , ^{13}C , and ^{19}F NMR spectra, were obtained at 600 MHz at $60\text{ }^\circ\text{C}$ using a JNM-ECA600 FT NMR spectrometer (JEOL Ltd.). The use of a double NMR tube, purchased from Shigemi Corp. (Catalog NO. SC-002), prevented the sample from mixing with the external standard. Traces of dimethyl

sulfoxide- d_6 (Cambridge Isotope Laboratories, Inc.) were placed in the outer tube (5.2 mm ϕ) and $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ was added to the internal tube (5.0 mm ϕ). The PGSE-NMR measurements were also performed at 60 and 75 °C using the same equipment. The self-diffusion coefficients of each component in $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ were measured using a simple Hahn spin echo sequence and analyzed using the Stejskal equation; $\ln(I/I_0) = -D(\gamma g \delta)^2(\Delta - \delta/3)$, where I is the echo signal intensity, I_0 is the initial echo signal intensity, D is the self-diffusion coefficient, γ is the gyromagnetic ratio ($2.67515 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$ for ^1H and $2.51716 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$ for ^{19}F), g is the amplitude of the gradient pulses, δ is the duration of the gradient pulses, and Δ is the interval between the leading edges of the gradient pulses.²³ The g values used were in the range 20–280 mT m $^{-1}$ at both temperatures, δ was 8 ms, and the value of Δ was 100 ms.

The conductivity of the electrolyte was determined by electrochemical impedance spectroscopy (Bio-Logic Science Instruments SAS, VSP-300) using stainless steel electrodes. The cell constant was calibrated with 0.1 and 1 mol dm $^{-3}$ KCl aqueous solutions. The measurement was carried out in a thermostatic chamber (Espec Co., SU-222) in the temperature range of 10 to 90 °C. Viscosity measurements were performed in

the same temperature range as conductivity measurements using a viscometer (Kyoto Electronics Manufacturing Co., Ltd., EMS-1000). Using the measured values of weight and volume, density was calculated to be 1.15 g cm^{-3} .

Thermal gravimetric analysis (TGA) was conducted for $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$, $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$, pure 18C6, and the equimolar mixture of HTf_2N and H_2O ($\text{HTf}_2\text{N}\cdot\text{H}_2\text{O}$) with the sweeping rate of $5 \text{ }^\circ\text{C min}^{-1}$, using Rigaku Thermo plus Evo-2 TG-DTA8122 instrument in dry air atmosphere. Metallic aluminum pans were used for $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$, $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$, and pure 18C6, and alumina pan for $\text{HTf}_2\text{N}\cdot\text{H}_2\text{O}$. 10 mg sample was placed on the pan and alumina powder was used as a standard.

Results and Discussion

Synthesis of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$. The equimolar mixture of 18C6 and $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ was a colorless liquid at RT. Table I shows the chemical analysis data for H, C, N, F, and S, which were consistent with the suggested formulation $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$, within $\pm 0.2 \text{ wt\%}$ of the calculated value. The H_2O content of the complex was 2.15 wt%, as

analyzed by Karl-Fischer coulometric titration, and in good agreement with the calculated value of 2.18 wt%. These quantitative analysis results support that the complex was $18C6:H_2O:HTf_2N = 2:1:1$ by mole.

Figure 1 displays the DSC curves for $[H_3O^+ \cdot (18C6)_2]Tf_2N$. The glass transition occurred at $-55\text{ }^\circ\text{C}$ and there was no melting point. Since the melting point for $[H_3O^+ \cdot 18C6]Tf_2N$ is $68\text{--}70\text{ }^\circ\text{C}$,⁷ this glass transition was caused because of dilution with 18C6.

Characterization of $[H_3O^+ \cdot (18C6)_2]Tf_2N$. Figure 2 shows a set of Raman spectra, where $[H_3O^+ \cdot (18C6)_2]Tf_2N$ displayed a peak at 875 cm^{-1} that indicated a change in the COC stretching and CH_2 rocking modes of 18C6 as a result of complex formation, similar to the case of $[H_3O^+ \cdot 18C6]Tf_2N$ and alkali metal ether complexes.^{7,24–30} A broad band between 750 and 850 cm^{-1} were observed in both $[H_3O^+ \cdot 18C6]Tf_2N$ and $[H_3O^+ \cdot (18C6)_2]Tf_2N$. According to Bühl *et al.*, the computed Raman bands for $[H_3O^+ \cdot 18C6]$ complex between 800 cm^{-1} and 900 cm^{-1} appear at B1 (860 cm^{-1}), B2 (828 cm^{-1}), B3 (810 cm^{-1}), and B4 (803 cm^{-1}), with the peak ratio $22:1:3:6$.³¹ We believe that the B1 band corresponds to a band centered at around 875 cm^{-1} and the other bands to a single broad band between 780 and 850 cm^{-1} , and these area ratio, estimated by Gaussian curve fitting (see Figure 2b), is $1:0.54 (= 22:(1+3+6))$, which agrees the computed result. Therefore, the broad band in $[H_3O^+ \cdot 18C6]Tf_2N$ does *not* belong to free 18C6 but to

$[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ complex. On the other hand, in $[\text{H}_3\text{O}^+\cdot (18\text{C6})_2]\text{Tf}_2\text{N}$, the ratio of a band centered at around 875 cm^{-1} to a broad band between 750 and 850 cm^{-1} is 1:2.2, much larger than 1:0.54. The larger value resulted not only from bound $[\text{H}_3\text{O}^+\cdot (18\text{C6})]$ complex but also from free 18C6, evidencing the presence of “free” 18C6 molecules in $[\text{H}_3\text{O}^+\cdot (18\text{C6})_2]\text{Tf}_2\text{N}$. In order to conduct more quantitative analysis, Raman measurements of $[\text{H}_3\text{O}^+(18\text{C6})_n]\text{Tf}_2\text{N}$ with $1 < n < 2$ are necessary, which are our future works. Notably, in both $[\text{H}_3\text{O}^+\cdot (18\text{C6})_2]\text{Tf}_2\text{N}$ and $[\text{H}_3\text{O}^+\cdot 18\text{C6}]\text{Tf}_2\text{N}$, the bands for Tf_2N^- anions centered at 741 cm^{-1} had no shoulder peaks and exhibited a similar full width of half maximum (fwhm) compared to our previous report,³² indicating that the Tf_2N^- anions were “free” and not present as complex anions such as $[\text{H}(\text{Tf}_2\text{N})_2]^-$.³³

The ν_1 – ν_4 bands in Fig. 3a proved the existence of H_3O^+ ; these characteristic bands readily established the presence of H_3O^+ with 18C6.^{34,35} The ν_1 and ν_3 stretching modes gave a very broad band centered at 2880 cm^{-1} , which overlapped with the sharper maximum at 2880 cm^{-1} arising from the C–H stretching motions of 18C6. The ν_4 band at 1650 cm^{-1} was attributed to the bending mode and the band at 2200 cm^{-1} was the first harmonic of ν_2 , i.e., the symmetric bending mode. The ν_2 band at 1100 cm^{-1} was not clearly observed because of overlapping with a strong band from 18C6.

The formation of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ was not clearly observed in the IR spectra (see Fig. 3b).

In our previous results, the COC stretching absorption for pure 18C6 was also seen as a

broad band at 1125 cm^{-1} , which disappeared and split into sharp bands at 1138 and 1091 cm^{-1} because of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ formation.^{7,34} In the case of $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$, the absorptions for both pure 18C6 and $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ overlapped.

These Raman and IR results strongly suggest that $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$ consists of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$, Tf_2N^- , and free 18C6 in the liquid state. Therefore, $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$ is a concentrated acid solution with free solvents rather than a hydronium solvate IL, based on the determination of the solvate IL.²⁴

The following NMR results support the results of chemical analysis, DSC, Raman, and IR measurements; although the results of ^1H and ^{13}C NMR for a different sample of $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$ were reported previously,⁸ those for the present sample are given in this article: The ^1H NMR spectrum (Fig. 4a) showed only two signals at 11.23 and 3.22 ppm, corresponding to H_3O^+ and CH_2 of 18C6, respectively. The peak area ratio was 1:16, which was in good agreement with the theoretical proton ratio for H_3O^+ and two 18C6 (or $\text{C}_{24}\text{H}_{48}\text{O}_{12}$). The signal for H_3O^+ in $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$ was shifted to a lower magnetic field than that in the spectrum of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]\text{Tf}_2\text{N}$. This indicated that the addition of 18C6 changed the chemical environment of H_3O^+ to a more positive charge.

The ^{13}C NMR spectrum (Fig. 4b) displayed a singlet for the 18C6 ligands (69.75 ppm) and a quartet for CF_3 of Tf_2N^- anions (122.96, 120.83, 118.69 and 116.55 ppm; peak area ratio of 1:3:3:1) with a peak area ratio of 12:1, which agreed with the theoretical ^{13}C ratio of two 18C6 to Tf_2N^- , i.e., $\text{C}_{24}\text{H}_{48}\text{O}_{12}:(\text{CF}_3\text{SO}_2)_2\text{N} = 24:2$. The results of ^1H and ^{13}C NMR measurements suggest that free and bound 18C6 could not be detected independently within the NMR measurement timescale.

In Fig. 4c, ^{19}F NMR spectrum exhibited a singlet at -79.57 ppm. In the case of pure HTf_2N , its signal for ^{19}F appeared at -76.0 ppm.³⁶ This indicates that ^{19}F for $[\text{H}_3\text{O}^+\cdot 18\text{C6}]\text{Tf}_2\text{N}$ was more negatively charged than that for pure HTf_2N , and that the precursor HTf_2N was not included in $[\text{H}_3\text{O}^+\cdot (18\text{C6})_2]\text{Tf}_2\text{N}$.

Self-diffusion coefficients. Figures 5a and 5b show the plots of echo signal attenuation on the basis of the Stejskal equation for 18C6 (red circles), Tf_2N^- (blue circles), and H_3O^+ (black circles) of $[\text{H}_3\text{O}^+\cdot (18\text{C6})_2]\text{Tf}_2\text{N}$ at 60 and 75 °C. As shown, the plots had a linear relationship. According to the Stejskal equation, the gradients of the fitted lines are proportional to the diffusion coefficients. Table II lists the estimated values of self-

diffusion coefficients for $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$ and $[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$. For $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$, the diffusion coefficient of H_3O^+ was almost the same as those of 18C6 and Tf_2N^- . Consequently, H_3O^+ moved as fast as 18C6 and Tf_2N^- in $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$, while H_3O^+ moved 1.5 times faster than 18C6 and Tf_2N^- in $[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$. In other words, the fast proton conduction of the hydronium solvate IL was suppressed by dilution. Notably, the self-diffusion coefficients of 18C6 and Tf_2N^- for $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$ at 60 °C were quite similar to those for $[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$ at 75 °C, and of $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$ at 75 °C were quite similar to those of $[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$ at 85 °C. In the case of common protic ILs,^{10–12} the Grotthuss-like conduction of H^+ is promoted by dilution, while ligands move faster when they are added to common solvate ILs.²⁴ Consequently, in terms of the effect of dilution, the hydronium solvate IL is distinguished not only from protic ILs but also from the previously reported solvate ILs.

Walden plot. A plot of molar conductivity ($\Lambda_{\text{imp}} / \text{S cm}^2 \text{ mol}^{-1}$) vs. fluidity ($\eta^{-1} / \text{Poise}^{-1}$),

i.e., the Walden plot, is displayed in Fig. 6. The molar conductivity Λ_{imp} of the solution is

defined as follows; $\Lambda_{\text{imp}} = M\sigma/d$, where σ is the conductivity measured by the electrochemical impedance method, d is density of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ (1.15 g cm^{-3}), and M is molecular weight (827.8 g mol^{-1}). The ionicity on the basis of Walden plot is expressed as $\Lambda_{\text{imp}}/\Lambda_{\text{ideal}}$, where both Λ_{imp} and Λ_{ideal} are the molar conductivities.³⁷ The molar conductivity, Λ_{ideal} , is the ideal molar conductivity at a given fluidity (η^{-1}) of an ideal KCl aqueous solution. In other words, the absolute value of Λ_{ideal} is equal to that of η^{-1} . The values of $\Delta W = \log(\Lambda_{\text{imp}}/\Lambda_{\text{ideal}})$, the vertical difference from the KCl ideal line in the Walden plot, were -0.33 at 60°C and -0.34 at 75°C , resulting in $\Lambda_{\text{imp}}/\Lambda_{\text{ideal}} = 0.46$ at both temperatures. Note that although the ionicity had been regarded as the degree of cation-anion dissociation,³⁸ the understanding of the ionicity of ionic liquids is further deepened.³⁹

Temperature dependence of η and σ . Figure 9 shows the temperature dependence of viscosity ($\eta/\text{mPa s}$) and ionic conductivity ($\sigma/\text{S cm}^{-1}$) of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ in the temperature range of 10 to 90°C . As these plots showed convex-curved profiles, the temperature-dependent conductivity and viscosity could be fitted using the empirical

Vogel-Fulcher-Tamman (VFT) equation; $\sigma = \sigma_0 \exp[-BT_0/(T-T_0)]$ for conductivity and $\eta = \eta_0 \exp[BT_0/(T-T_0)]$ for viscosity, where σ_0 , η_0 , B , and T_0 are adjustable parameters.⁴⁰

These fitting parameters are listed in Table III. The VFT-type parameters of viscosity and ionic conductivity were similar, indicating that the temperature dependence of viscosity dominated that of ionic conductivity.

Dilution effect for the hydronium solvate IL. Table IV summarizes the viscosities and conductivities of $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ (at 60 and 75 °C) and $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ (at 75 and 85 °C). Comparing these values of $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ at 60 °C with those of $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ at 85 °C, it was evident that the conductivity of the latter was 1.5 times that of the former, while both had similar viscosities. On the other hand, conductivities of both $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ and $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ were almost the same at 75 °C, while the viscosity of the former was about half that of the latter and each diffusion coefficient of H_3O^+ , 18C6, and Tf_2N^- at 75 °C in $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ was larger than that in $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$, as shown in Table II. The higher conductivity of $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ compared to that of $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ was a result of the faster proton conduction in

the former.

The ionicity, expressed as $\lambda_{\text{imp}}/\lambda_{\text{NMR}}$, was also estimated by means of impedance and PGSE-NMR measurements, where both λ_{imp} and λ_{NMR} are molar conductivities. The molar conductivity, λ_{imp} , of the solution is defined as above. The molar conductivity λ_{NMR} is given by the Nernst-Einstein equation, $\lambda_{\text{NMR}} = F^2/RT(D_{\text{H}_3\text{O}^+} + D_{\text{Tf}_2\text{N}^-})$, where F is Faraday constant, R is the gas constant, T is the absolute temperature, and $D_{\text{H}_3\text{O}^+}$ and $D_{\text{Tf}_2\text{N}^-}$ are the self-diffusion coefficients of H_3O^+ and Tf_2N^- , respectively, measured by PGSE-NMR.²⁵ Table V lists the calculated ionicities for $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ at 60 and 75 °C.

Table V also summarizes the proton transference numbers at 60 and 75 °C using $D_{\text{H}_3\text{O}^+}$

and $D_{\text{Tf}_2\text{N}^-}$. According to Harris,⁴¹ the use of equation $t_{\text{H}_3\text{O}^+} = (D_{\text{H}_3\text{O}^+}/D_{\text{H}_3\text{O}^+} + D_{\text{Tf}_2\text{N}^-})$ is at

best an alternative way of saying one species diffuses more rapidly than the other. While

H_3O^+ apparently diffuses faster than Tf_2N^- in $[\text{H}_3\text{O}^+(\text{18C6})]\text{Tf}_2\text{N}$ because transference

number is more than 0.5, it is likely that H_3O^+ moves as fast as Tf_2N^- because $t_{\text{H}_3\text{O}^+}$ is

nearly equal to 0.5 in $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$.

It has been shown that the diffusion coefficients of H_3O^+ and 18C6 are almost the same

in $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$. We propose, however, that this conduction mechanism is

different from the “ordinary” vehicle mechanism. Given an ordinary vehicle mechanism in $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$, H_3O^+ and two 18C6 ligands would be bound to form a sandwich complex and move together. A possibility of a $18\text{C}6\text{--H}_3\text{O}^+\text{--}18\text{C}6$ sandwich complex, however, can be rejected because a sandwich complex of H_3O^+ between two crown ether ligands is formed only when the crown ether has a smaller cavity than that of 18C6.³⁴ The TGA results also deny the possibility of this sandwich complex (see Figure 8). Given 2 to 1 sandwich complexes in $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$, the hydronium ion would form hydrogen bonds with two oxygens of one 18C6 ligand and with one oxygen of the other 18C6, as well as the real sandwich complex.³⁴ The hydrogen bonds of the sandwich complexes should be weaker than $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$, and the weight loss of TGA for $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ would start at much lower temperature. We found, however, that the TGA curves are similar to each other (see Figs. 8a and 8b). We also speculate that the COC Raman band would not be similar to that of $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ due to weaker coordination if such sandwich complex were exist in $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$. The value of fwhm of the band in $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ is actually 17.9 ± 0.4 , similar to that of $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ (16.5 ± 0.3).

Since the NMR and Raman results proved that the free and bound 18C6 molecules exchange very fast, protons make round trips between the two 18C6 in this system. In fact, the fwhm value of the ^1H NMR signals of 18C6 in $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ (0.0108 at 60 °C) was approximately 25% of $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ (0.0414 at 75 °C), even though the viscosity of the former (33.9 mPa s at 60 °C) was about 80% of the latter (42.9 mPa s at 75 °C). Thus, the narrow signals of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ were attributable to the faster ligand exchange of chemical states caused by the “localized exchange”. Consequently, we propose that the added solvents induce local proton exchange (i.e., round trip of protons) rather than promoting a cooperative proton relay of the hydronium solvate IL.

Conclusions

In this work, the physicochemical properties of an equimolar mixture of solvent and hydronium solvate ionic liquid, $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$, were studied. While protons of H_3O^+ moved faster than 18C6 ligands in $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$, the addition of the 18C6 solvent suppressed the fast proton conduction. The NMR spectroscopy results showed that as the free 18C6 ligands and coordinated ones underwent fast exchange in the diluted

sample, the proton exchange became localized between the neighboring 18C6 ligands and terminated the cooperative proton relay of $[\text{H}_3\text{O}^+ \cdot 18\text{C6}]\text{Tf}_2\text{N}$. The protonic properties of $[\text{H}_3\text{O}^+ \cdot (18\text{C6})_n]\text{Tf}_2\text{N}$ with $1 < n < 2$ are of special interest. Identification and rationalization of proton transfer in a series of concentrated $\text{H}_3\text{O}^+ - 18\text{C6}$ electrolytes can provide the guidelines for designing new electrolyte systems.

Acknowledgments

This work was supported financially by Grants-in-Aid for Scientific Research (B) (No.19H02490: A. K.) from the Japan Society for the Promotion of Science. A. K. also thanks the Joint Usage/Research Program on Zero-Emission Energy Research, Institute of Advanced Energy, Kyoto University (ZE31A-1).

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Table I. Result of chemical analysis for $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$.

Element	H (%)	C (%)	N (%)	F (%)	S (%)
Experimental	6.21	37.59	1.76	13.92	7.75
Calculated	6.17	37.73	1.69	13.78	7.74

Table II. Diffusion coefficients of H_3O^+ , 18C6, and Tf_2N^- at 60 and 75 °C for $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$, and at 75 and 85 °C for $[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$.

Mixture	Temperature	$D_{\text{H}_3\text{O}^+}$	$D_{18\text{C6}}$	$D_{\text{Tf}_2\text{N}^-}$
	[°C]	[$10^{-7} \text{ cm}^2 \text{ s}^{-1}$]	[$10^{-7} \text{ cm}^2 \text{ s}^{-1}$]	[$10^{-7} \text{ cm}^2 \text{ s}^{-1}$]
$[\text{H}_3\text{O}^+\cdot(18\text{C6})_2]\text{Tf}_2\text{N}$	60	2.4	2.7	2.6
	75	3.9	4.1	4.1
$[\text{H}_3\text{O}^+\cdot 18\text{C6}]\text{Tf}_2\text{N}$	75	3.6	2.4	2.6
	85	6.0	3.9	4.0

Table III. VFT fitting parameters for ionic conductivity and viscosity.

	σ_0 or η_0	B	T_0 [K]	BT_0 [K]
Conductivity	0.445 [S cm ⁻¹]	1.82	189	344
Viscosity	0.199 [mPa s]	1.51	199	300

Table IV. Viscosities and conductivities of $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$ (this work, at 60 and 75 °C), and $[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$ (ref. 7; at 75 and 85 °C).

Mixture	Temperature [°C]	Viscosity [mPa s]	Conductivity [mS cm ⁻¹]
$[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$	60	33.9	1.90
	75	20.3	2.67
$[\text{H}_3\text{O}^+\cdot 18\text{C}6]\text{Tf}_2\text{N}$	75	42.9	2.36
	85	32.3	3.05

Table V. Ionicities and transference numbers of $[\text{H}_3\text{O}^+\cdot(18\text{C}6)_2]\text{Tf}_2\text{N}$ at 60 and 75 °C.

Temperature [°C]	Ionicity	Transference number
	$A_{\text{imp}}/A_{\text{NMR}}$	$t_{\text{H}_3\text{O}^+}$
60	0.78	0.48
75	0.88	0.49

Figure 1. DSC curves for $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$.

Figure 2. (a) Raman spectra between 700 and 900 cm^{-1} of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ (at room temperature), $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ (at 75 °C), and pure 18C6 (at 60 °C), and (b) Raman spectra (red curves) and Gaussian fits (blue curves) between 760 and 900 cm^{-1} for $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$ (upper panel) and $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ (lower panel).

Figure 3. IR spectra of $\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$, $[\text{H}_3\text{O}^+\cdot\text{18C6}]\text{Tf}_2\text{N}$, and pure 18C6 measured at room temperature: (a) high-wavenumber region from 1600 to 4000 cm^{-1} and (b) low-wavenumber region from 800 to 1400 cm^{-1} .

Figure 4. (a) ^1H , (b) ^{13}C , and (c) ^{19}F NMR spectra of $[\text{H}_3\text{O}^+(\text{18C6})_2]\text{Tf}_2\text{N}$ at 60 °C.

Figure 5. Plots and best-fit lines of echo signal attenuation on the basis of the Stejskal equation for 18C6 (red circles), Tf_2N^- (blue circles), and H_3O^+ (black circles) at (a) 60 °C and (b) 75 °C.

Figure 6. Walden plots for $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$ (squares) and $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$ (triangles; ref. 7).

Figure 7. Plots and best-fit lines of the temperature dependence of ionic conductivities (open circles) and viscosities (closed circles) of $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$.

Figure 8. TGA curves for (a) $[\text{H}_3\text{O}^+ \cdot (18\text{C}6)_2]\text{Tf}_2\text{N}$, (b) $[\text{H}_3\text{O}^+ \cdot 18\text{C}6]\text{Tf}_2\text{N}$, (c) pure 18C6, and (d) $\text{HTf}_2\text{N} \cdot \text{H}_2\text{O}$.















